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Electron cyclotron resonance plasma etching of oxides and SrS and ZnS-based electroluminescent materials for flat panel displays

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A number of different plasma chemistries have been investigated for the etching of oxides (indium tin oxide for conductive electrodes; alumina/titania and Al_2O_3 for insulators) and phosphors (SrS, ZnS) used in thin film electroluminescent displays. Under high ion density conditions, such as in an electron cyclotron resonance source, maximum etch rates above 1500 Å/min are obtained for ZnS in Cl_2/Ar , BCl_3/Ar , and SF_6/Ar , for SrS in SF_6/Ar and $\text{CH}_4/\text{H}_2/\text{Ar}$, for ITO in $\text{CH}_4/\text{H}_2/\text{Ar}$ and for ATO in SF_6/Ar . The etching is ion activated under most conditions, producing good feature anisotropy. Near-surface stoichiometry could generally be maintained on the etched surfaces of all materials except SrS where we invariably detected strong preferential loss of S. An optimized process for etching a typical metal-insulators-semiconductor-insulator-metal stack would involve switching plasma chemistries for each individual layer, but we have successfully patterned such a stack using only the $\text{CH}_4/\text{H}_2/\text{Ar}$ chemistry. © 1998 American Vacuum Society.
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I. INTRODUCTION

The basic structure of a thin film electroluminescent (EL) display device involves a phosphor layer (typically ZnS, SrS or doped alkali-earth thiogallates) sandwiched by thin film dielectrics (typically Al_2O_3 or alumina/titania, ATO) which acts as current limiters.¹⁻³ A transparent conducting electrode material is deposited on the viewing side, and indium tin oxide (ITO) is the most common choice. The backside of the stack is contacted with a metal such as TiW or Al. The field strength required across the phosphor to produce light emission is substantial ($> 2 \times 10^6$ V/cm), and therefore the sandwiching dielectric layers are necessary to prevent deterioration of the phosphor.^{1,2}

Pattern transfer in these devices represents a major challenge, simply because there will always be at least three or four different materials which require etching.⁴ An obvious approach for plasma etch processes would be to employ a sequence of different gas chemistries, each optimized for a particular layer, and to monitor the progress of the etch front by laser reflectometry to control the switching in and out of these different gases. A common approach currently is to use a combination of wet chemical etching and ion milling for pattern transfer, but this is probably not the most efficient manufacturing mode if high throughput and yield are paramount. There have been a number of recent reports on reactive ion etching of display materials. ITO has been etched in plasma chemistries of CH_4/H_2 ,⁵ HBr ,⁶ Cl_2/Ar ,^{7,8} and HI ,^{9,10} and Al_2O_3 was etched in CF_4/O_2 .¹¹

The relatively recent advent of high ion flux plasma

sources offers the possibility of new etch regimes for materials with high bond strengths and/or involatile etch products,¹² such as those that compromise EL devices. In this paper we report the results of a parametric study of dry etch rates of ZnS, SrS, ATO, ITO, Al_2O_3 , and TiW in Cl_2 -, F_2 -, or CH_4/H_2 -based electron cyclotron resonance (ECR) discharges. Experimental variables were process pressure, source power (which controls ion flux), rf chuck power (which controls ion energy), and plasma composition. As expected, we found that the different materials etched at substantially different rates in these chemistries, and that no one particular plasma chemistry provided a completely satisfactory pattern transfer process. However, we were able to etch complete EL device stacks with the simple $\text{CH}_4/\text{H}_2/\text{Ar}$ chemistry in about 40 min. This chemistry has the advantage of being noncorrosive and thereby reduces the need for post-etch cleaning of the samples, and eliminates requirements for corrosive gas handling.

II. EXPERIMENT

The etch rates of the individual materials were determined on single layer sample deposited on Si substrates by either rf magnetron sputtering (SrS, ITO, and TiW)¹³ or by chemical vapor deposition (ZnS, ATO, and Al_2O_3).¹⁴

Some samples were patterned with AZ5214E photoresist in a resolution test pattern, and etch rates were measured by stylus profilometry of the feature depth after removal of the resist in acetone or an O_2 plasma. Unpatterned samples were also exposed to the various plasma chemistries and subsequently examined by Auger electron spectroscopy (AES).

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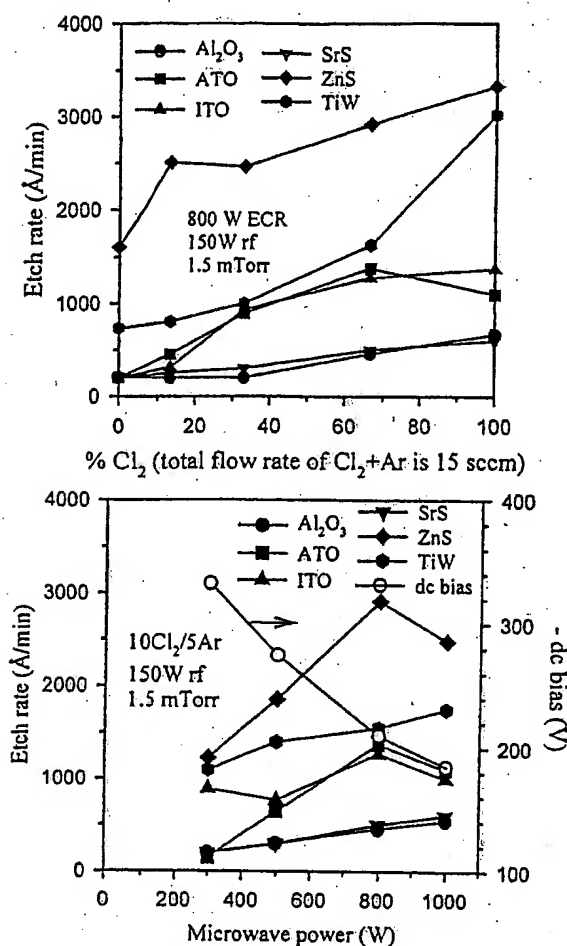


FIG. 1. Etch rates of display materials as a function of (top) Cl₂ percentage in Cl₂/Ar discharges (800 W source power, 150 W rf chuck power, 1.5 mTorr), or (bottom) as a function of source power in 10Cl₂/5Ar, 1.5 mTorr, 150 W rf chuck power discharges.

The etching was performed in a Plasma Therm 770 SLR system in which the discharge is generated in a low profile ASTEX 4400 ECR source (0–1000 W at 2.45 GHz), and the sample chuck power is separately biased with rf (13.56 MHz) power.¹⁵ The chuck power was varied from 50 to 450 W, and the resultant dc self-bias was a function of both plasma chemistry and microwave power—typical values were –30 to –85 V at 50 W rf to –250 to –535 V at 250 W rf. The process pressure was varied from 1.5 to 10 mTorr by throttling the main pump (1500 ℓ s⁻¹ turbomolecular). The gases were either injected directly into the ECR source (Cl₂, BCl₃, SF₆, IBr, Ar, N₂, H₂) or into a gas distribution ring (CH₄) near the sample chuck. These cover the range of possible etch products that might be formed. Typical total gas flow rates were 15–40 standard cubic centimeters per minute.

III. RESULTS AND DISCUSSION

Figure 1 shows the effect of plasma composition (top) and ECR source power (bottom) on etch rates in Cl₂/Ar dis-

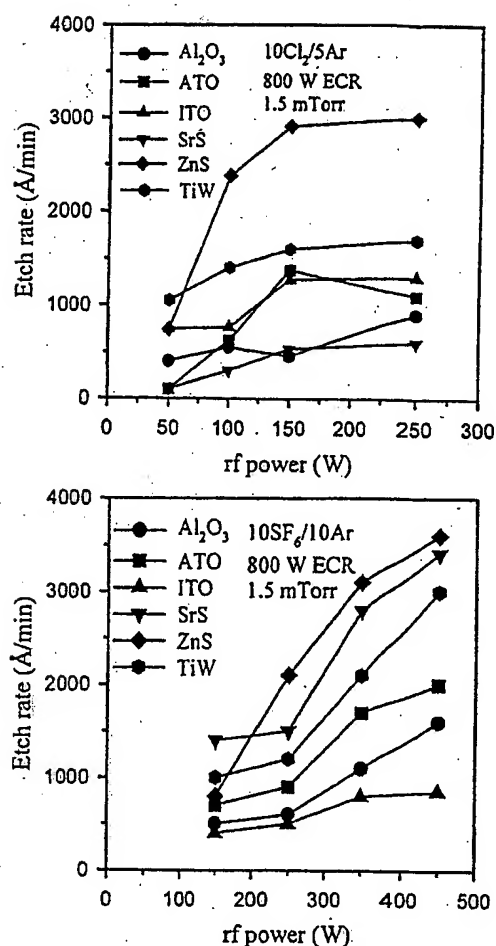


FIG. 2. Etch rates of display materials as a function of rf chuck power in 800 W source power, 1.5 mTorr discharges of either Cl₂/Ar (top) or SF₆/Ar (bottom).

charges. For all of the materials there is a significant amount of chemical enhancement in the etch rates, since these rates increase with Cl₂ percentage. This is an attractive feature not only from the viewpoint of faster rates, but also for improved selectivity with respect to mask materials and reduced redeposition on feature sidewalls relative to simple ion milling. Fairly similar trends were seen with BCl₃/Ar discharges, with the absolute rates being ~20% lower than for Cl₂/Ar. As the ECR source power is increased there is also a general trend for faster etch rates, even though as the ion density is increased, the induced dc bias on the sample electrode decreases (Fig. 1, bottom). This produces a reduction in etch rate for ATO, ZnS, and ITO.

The fact that ion energy as well as ion flux is important in determining etch rate is obvious in the data of Fig. 2. For all chemistries (we show results for Cl₂/Ar and SF₆/Ar as examples), we observed a general increase in rate as the rf chuck power was increased. In some cases the etch rates saturates, particularly in Cl₂/Ar (rf powers of 150–250 W correspond to induced dc voltages of approximately –125 to –140 V; the ion energy is the sum of this voltage plus plasma potential, which is roughly –20 V in these systems).

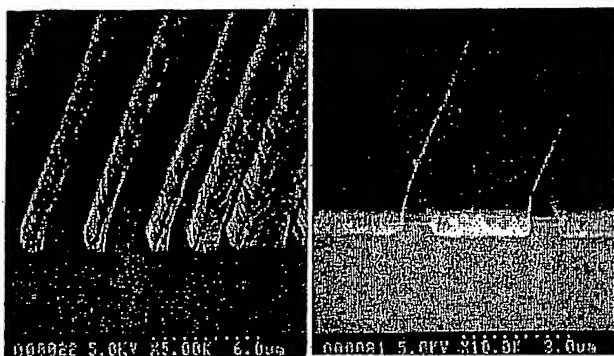


FIG. 3. SEM micrographs of features etched into (left) ITO using an SiO_2 mask and a $10\text{Cl}_2/\text{Ar}$, 1.5 mTorr, 150 W rf power, 800 W source power discharge, and (right) ITO/ATO stack using a photoresist mask and the same plasma conditions.

This is often observed in high ion density etching of electronic materials, and is usually ascribed to sputter-induced desorption of the active plasma species before they can react with the sample. The etch rates for ITO in $\text{CH}_4/\text{H}_2/\text{Ar}$ and $\text{CH}_4/\text{H}_2/\text{N}_2$ chemistries were typically $\sim 1000 \text{ \AA}/\text{min}$ at source powers of 800–1000 W and rf chuck powers of 250 W. The rates were typically around $250 \text{ \AA}/\text{min}$ under these conditions for the other materials (Al_2O_3 , ATO, SrS, ZnS, and TiW) in these chemistries.

Some typical scanning electron microscopy (SEM) micrographs of features produced by ECR etching are shown in Fig. 3. The features at the left were formed by Cl_2/Ar etching of ITO masked by SiO_2 , while these at the right were created by Cl_2/Ar etching through ITO into ATO using a photoresist mask. There is some degree of surface roughening in both cases, which is of less concern when etching through a full stack and ending on an etch-stop layer because with a suitable overetch one will obtain a smooth surface. While the SiO_2 mask holds up well to the Cl_2/Ar chemistry, there is clear erosion of the photoresist mask under these conditions.

We tried a variety of processes for etching a full EL stack (ITO/ATO/SrS/ATO, stopping on TiW), and a couple of typical SEM micrographs are shown in Fig. 4. The features at the top were formed using Cl_2/Ar etching and a photoresist mask, and even after etching the $\sim 2 \mu\text{m}$ thick structure, the morphology apparent on the underlying TiW is reasonably good. The micrograph at the bottom shows a feature in which sequential etches were done with $\text{CH}_4/\text{H}_2/\text{Ar}$ (for ITO), Cl_2/Ar (for ATO), SF_6/Ar (for SrS), Cl_2/Ar (for ATO), and $\text{CH}_4/\text{H}_2/\text{Ar}$ to etch partially into the TiW. While the process time for this sequence is around 25 min (i.e., an average rate for the whole stack of $800 \text{ \AA}/\text{min}$), we also obtained fairly similar results if $\text{CH}_4/\text{H}_2/\text{Ar}$ alone were used to etch the entire stack, with the only penalty being that the process time increased to ~ 40 min (i.e., an average rate for the whole stack of $500 \text{ \AA}/\text{min}$). Photoresist masks in general do not hold up well to high power ECR discharges, and

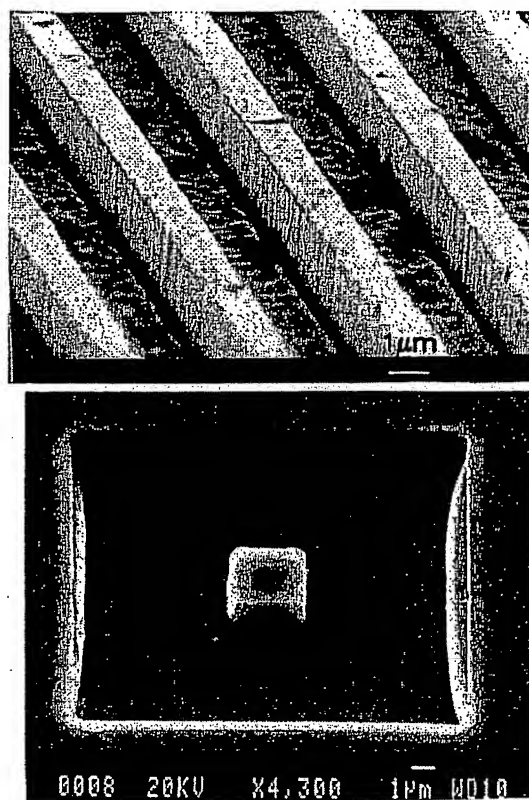


FIG. 4. SEM micrographs of features etched into EL device stack using (top) 800 W source power, 150 W rf, 1.5 mTorr Cl_2/Ar plasma. The resist mask has been removed, or (bottom) a sequence of $\text{CH}_4/\text{H}_2/\text{Ar}$, Cl_2/Ar , SF_6/Ar , Cl_2/Ar , and $\text{CH}_4/\text{H}_2/\text{Ar}$ discharges at 800 W source power, 1.5 mTorr, 150–250 W rf power discharges. The SiO_2 mask has been removed.

alternatives such as SiO_2 , SiN_x , or plated Ni are superior choices.

The near-surface stoichiometry of ZnS was a strong function of the chlorine neutral-to-Ar ion ratio in chlorine-based chemistries. Figure 5 shows AES surface scans before (top) and after (center and bottom) BCl_3/Ar etching with two different compositions. The $10\text{BCl}_3/5\text{Ar}$ plasma (center) retains the same Zn/S ratio as in the control sample, and the only major difference is the presence of B and Cl residues on the etched sample. At a plasma composition of $2\text{BCl}_3/13\text{Ar}$ (bottom) there is preferential loss of the lighter S, indicating an insufficient chlorine neutral concentrations. Most of the previous work on etching II–VI compounds has focused on the CH_4/H_2 chemistry, although the general result there is that the surface is left slightly group VI deficient.¹⁶

On all of the dry etched SrS samples we encountered surface charging, evidenced by distortion of the low energy end of the AES surface scans. Figure 6 shows results before and after etching in SF_6/Ar , which shows a strong F-residue signal. This same reduction in S signal was observed on all dry etched samples, regardless of the plasma chemistry used. Although analysis is problematic under these conditions, it appears that there is preferential loss of S in all cases, which

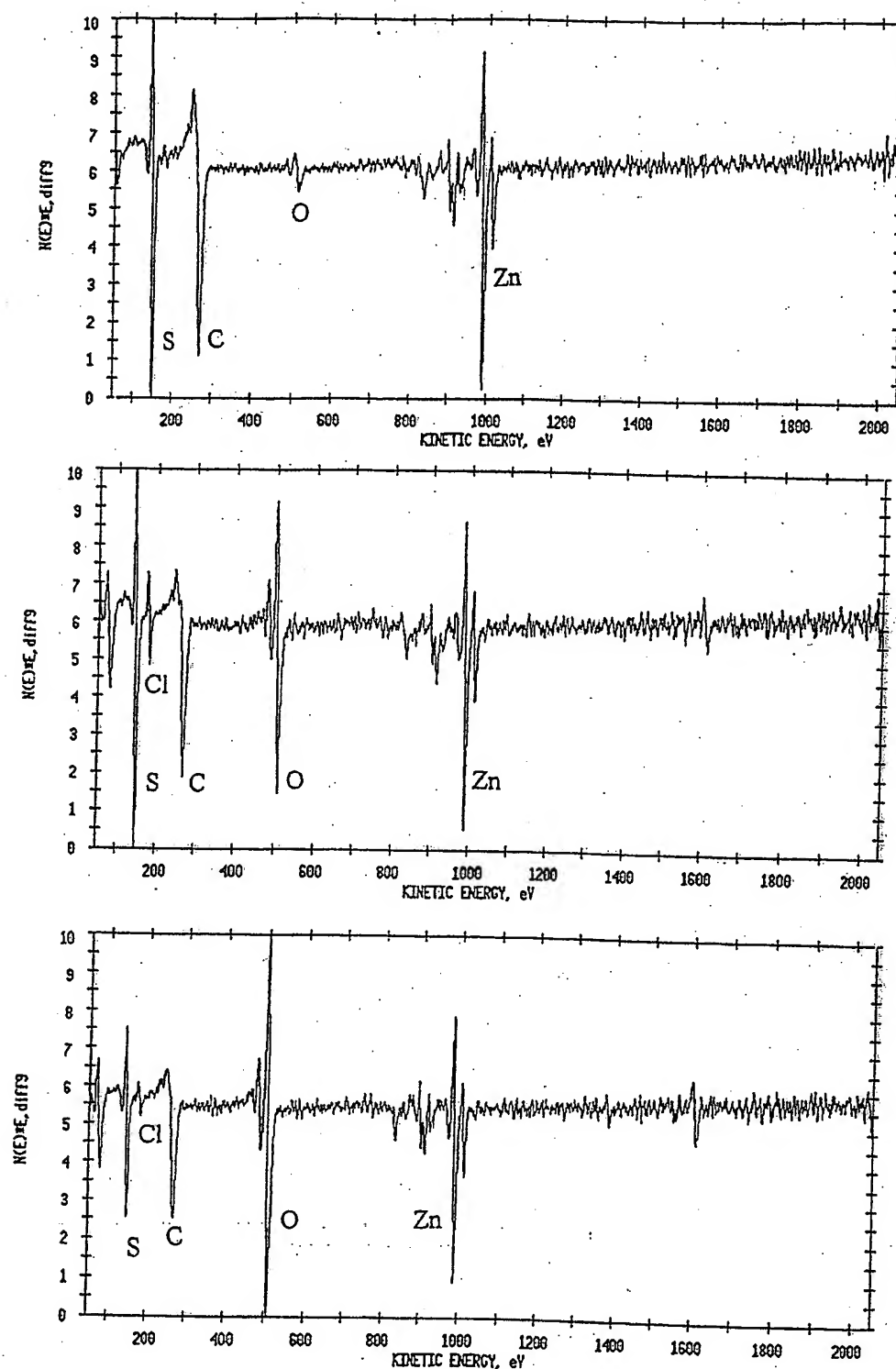


FIG. 5. AES surface scans of ZnS before (top) and after etching in $10\text{BCl}_3/5\text{Ar}$ (center) or $2\text{BCl}_3/\text{Ar}$ (bottom) discharges (800 W source power, 150 W rf power, 1.5 mTorr).

is not surprising given the fact that the S etch products in all chemistries are considerably more volatile than their Sr counterparts. For the other materials, we could generally maintain reasonable near-surface stoichiometrics in all of the plasma chemistries.

IV. SUMMARY AND CONCLUSIONS

The use of ECR plasma reactors produces what appear to be practical etch rates for current throughputs used in electroluminescent display device fabrication. A feature of most

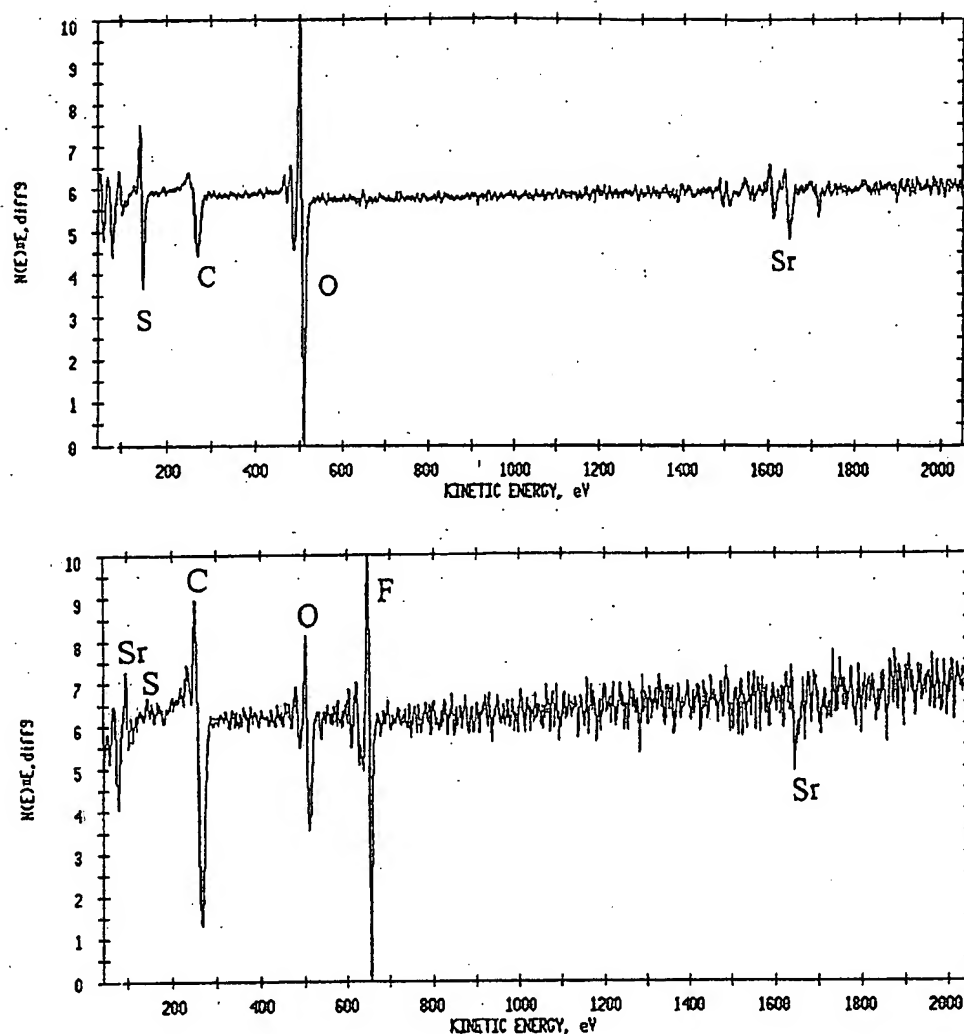


FIG. 6. AES surface scans of SrS before (top) and after (bottom) etching in 800 W source power, 150 W rf power, 1.5 mTorr SF_6/Ar discharges.

of these materials is their high average bond energy, and relatively low volatility of some of their potential etch products, making conventional etch processes difficult to use. Control of both ion energy and ion flux is important in designing etch processes for EL stacks.

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